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(54) **METHODS OF FORMING THROUGH SILICON VIA OPENINGS**

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- (\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 69 days.

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(52) **U.S. Cl.**

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(58) **Field of Classification Search**

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See application file for complete search history.

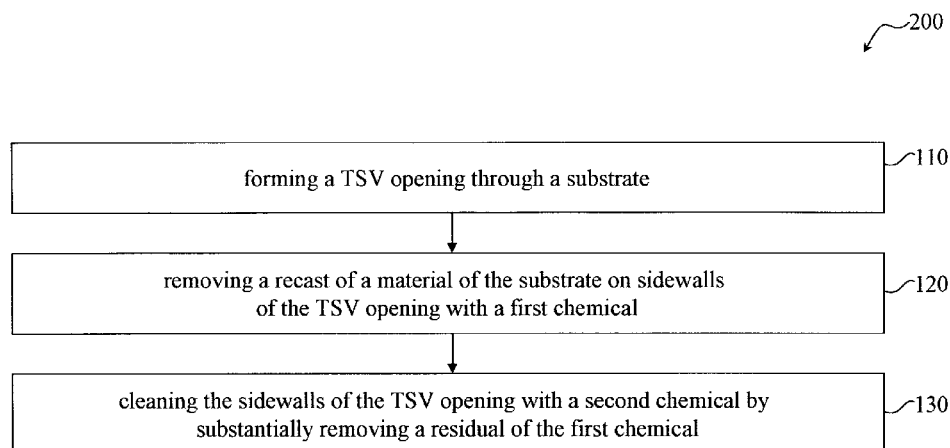
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(57) **ABSTRACT**

A method includes forming an opening in a substrate, and the opening completely extends through the substrate. A recast material is formed on sidewalls of the substrate exposed by the opening. A first chemical is applied in the opening to remove the recast material, wherein a residue of the first chemical remains on portions of the sidewalls after the applying of the first chemical. Moreover, A second chemical is applied in the opening to remove the residue of the first chemical, and the second chemical is different from the first chemical.

**15 Claims, 5 Drawing Sheets**



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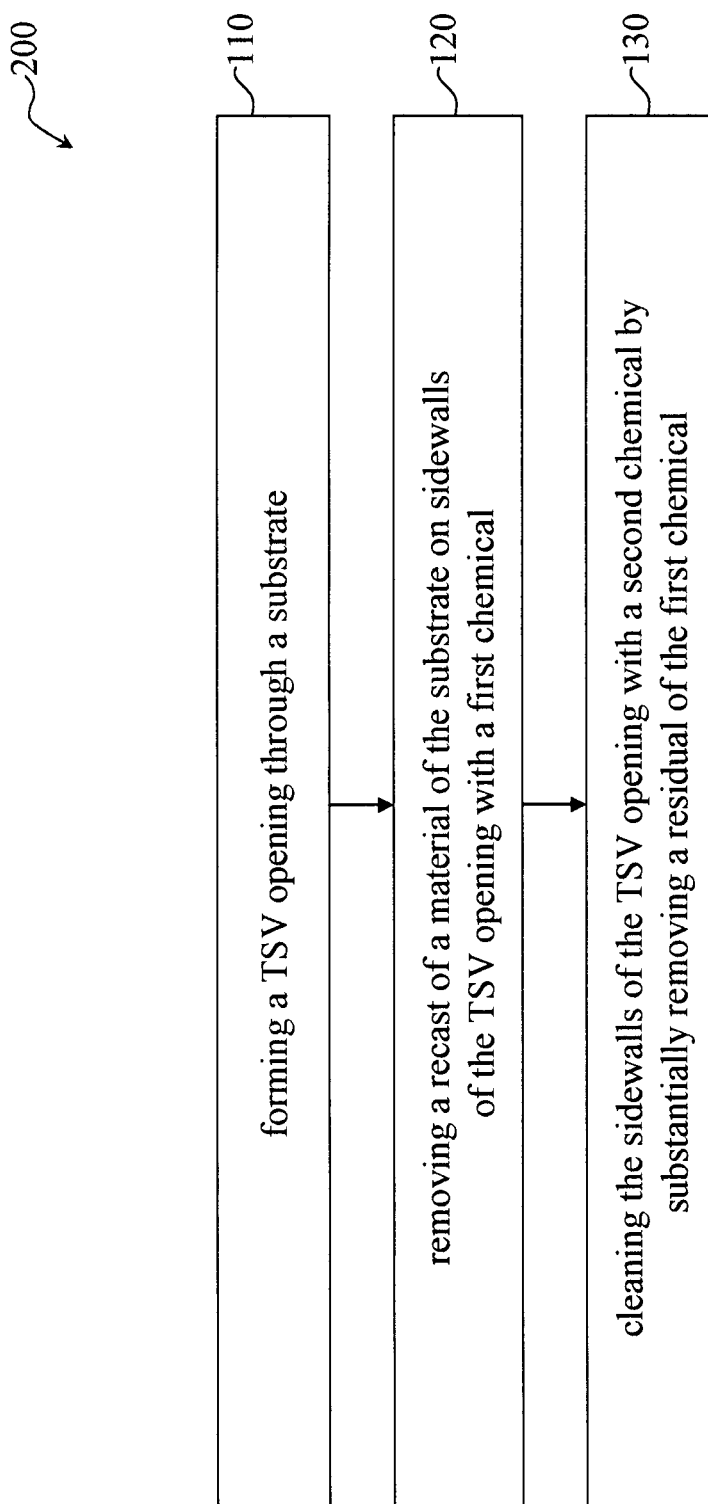


FIG. 1

200

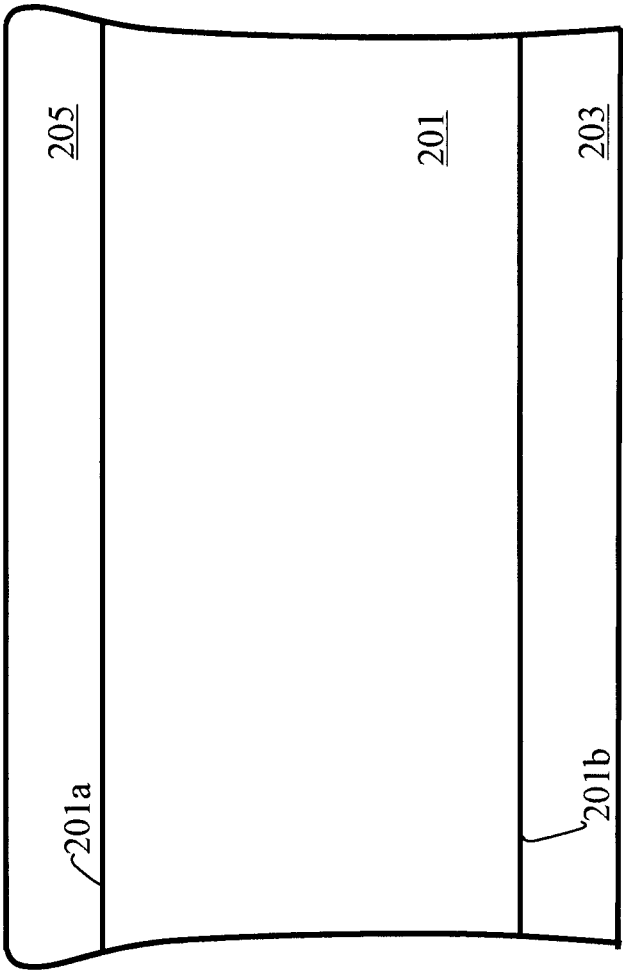


FIG. 2A

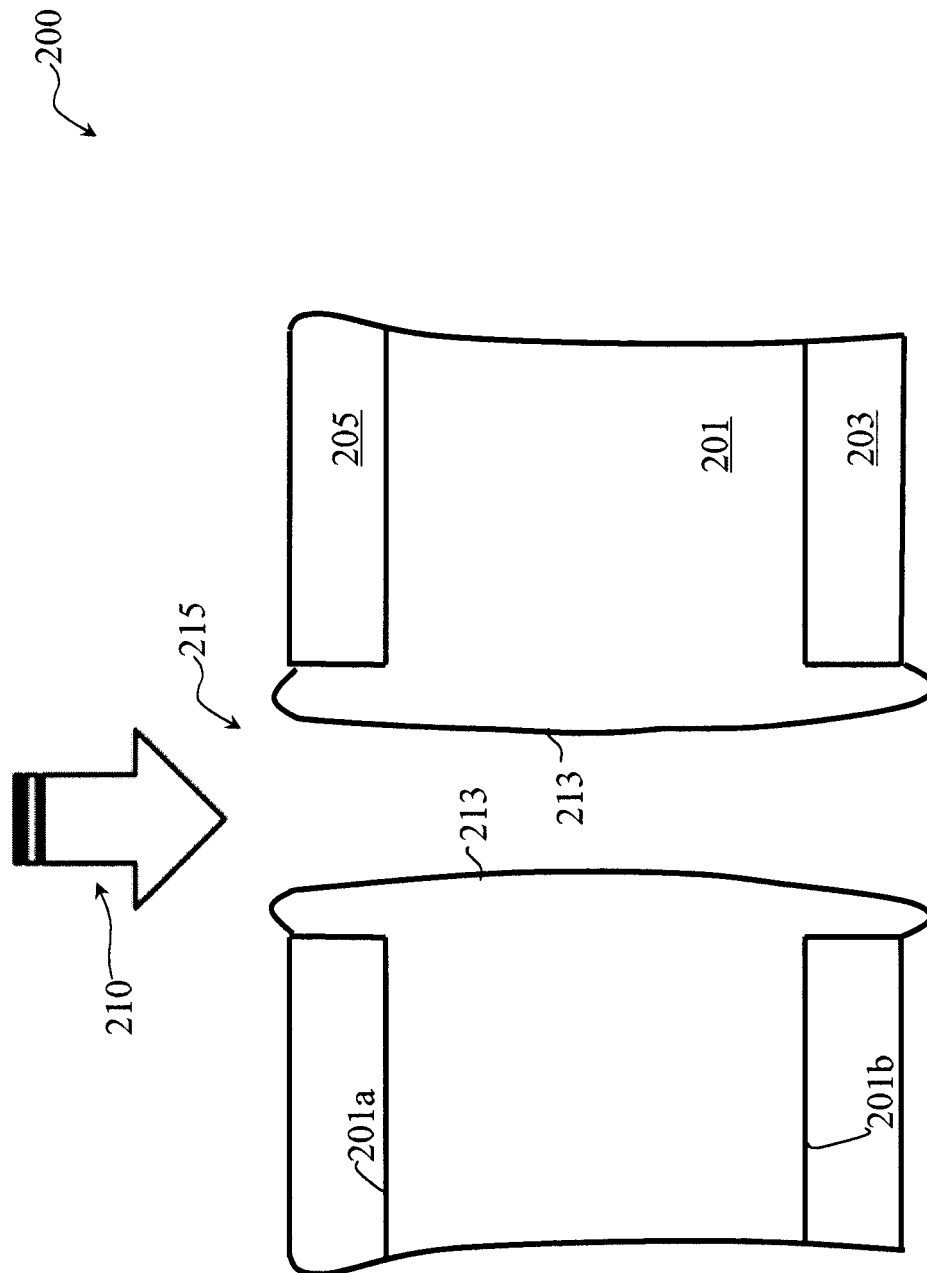


FIG. 2B

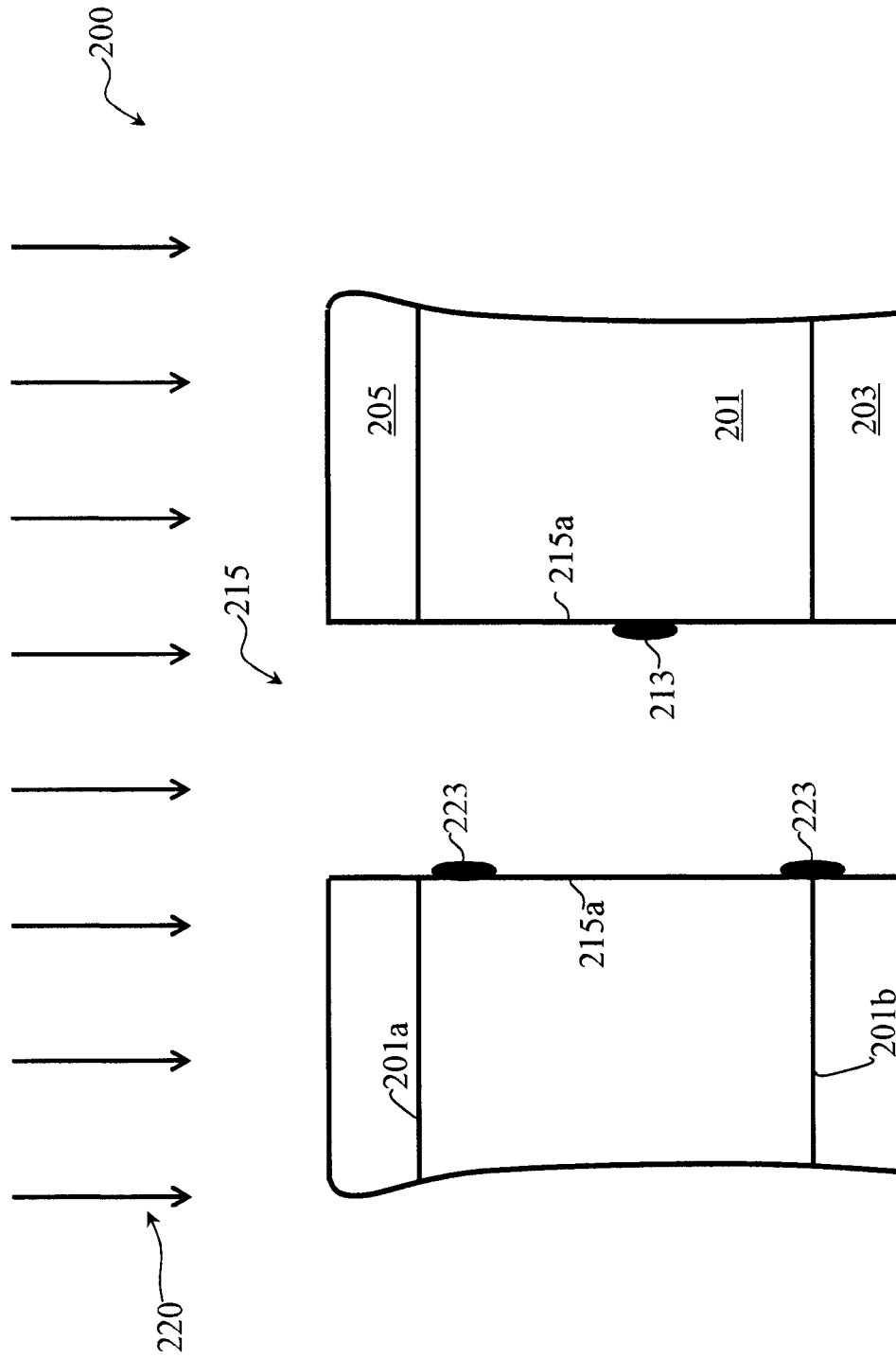


FIG. 2C

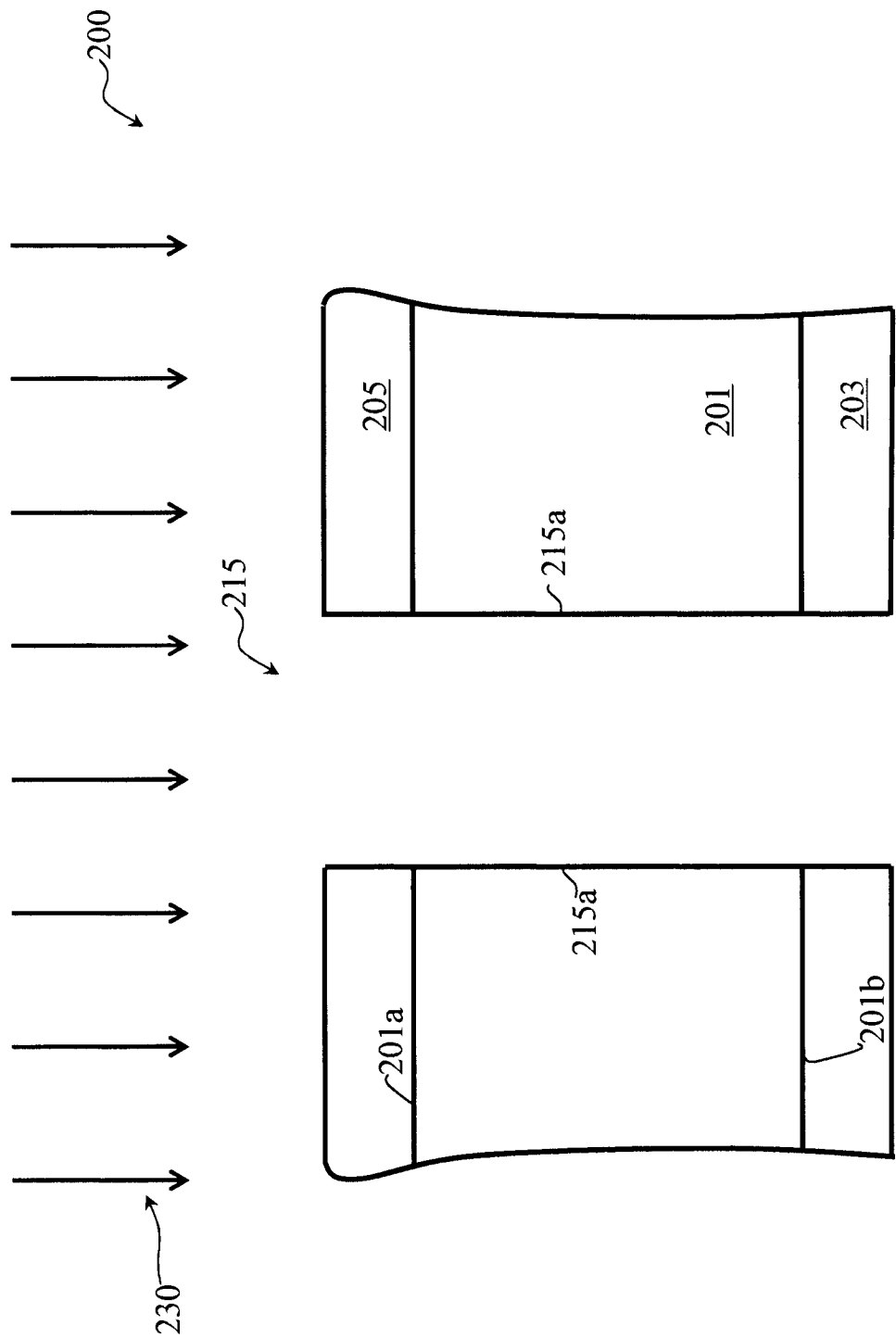


FIG. 2D

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## METHODS OF FORMING THROUGH SILICON VIA OPENINGS

### PRIORITY DATA

The present application is a continuation application of U.S. patent application Ser. No. 13/086,542, filed on Apr. 14, 2011, entitled "Methods of Forming Through Silicon Via Openings" now U.S. Pat. No. 8,716,128 issued May 6, 2014, the disclosure of which is hereby incorporated by reference in its entirety.

### TECHNICAL FIELD

The present disclosure relates generally to the field of semiconductor and, more particularly, to methods of forming through silicon via openings.

### BACKGROUND

Since the invention of the integrated circuit, the semiconductor industry has experienced continual growth due to continuous improvements in the integration density of various electronic components (i.e., transistors, diodes, resistors, capacitors, etc.). For the most part, this improvement in integration density has come from repeated reductions in minimum feature size, allowing for the integration of more components into a given area.

These integration improvements are essentially two-dimensional (2D) in nature, in that the volume occupied by the integrated components is essentially on the surface of the semiconductor wafer. Although dramatic improvements in lithography have resulted in considerable improvements in 2D integrated circuit formation, there are physical limits to the density that can be achieved in two dimensions. One of these limits is the minimum size needed to make these components. Also, when more devices are put into one chip, more complex designs are required.

Three-dimensional integrated circuits (3D IC) are therefore created to resolve the above-discussed limitations. In a conventional formation process of 3D IC, two wafers, each including an integrated circuit, are formed. The wafers are then bonded with the devices aligned. Deep vias are then formed to interconnect devices on the first and second wafers.

### BRIEF DESCRIPTION OF THE DRAWINGS

The present disclosure is understood from the following detailed description when read with the accompanying figures. It is noted that, in accordance with the standard practice in the industry, various features are not drawn to scale and are used for illustration purposes only. In fact, the numbers and dimensions of the various features may be arbitrarily increased or reduced for clarity of discussion.

FIG. 1 is a flowchart of an exemplary method of forming a through-silicon-via (TSV) opening through a substrate,

FIGS. 2A-2D are schematic cross-sectional views of forming a TSV opening in an integrated circuit during various fabrication stages.

### DETAILED DESCRIPTION

A method known to the applicants for forming TSV openings for 3D IC uses silicon hexafluoride ions ( $\text{SiF}_6^{2-}$ ) as an etching agent. It is found that the etching process results in the presence of scallops on sidewalls of the TSV openings. The step coverage of a liner or barrier/seed layer that is deposited

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on the scallop sidewalls of the TSV openings is impaired. The poor step coverage of the liner or barrier/seed layer damages electrical characteristics of conductive structures formed in the TSV openings.

Another method known to the applicants uses a laser ablation to remove silicon material of a silicon substrate, forming the TSV opening. However, it is found that the silicon particles and/or debris fall on the surface and sidewalls of the TSV openings, resulting in scallop-like roughened sidewall surfaces.

It is understood that the following disclosure provides many different embodiments, or examples, for implementing different features of the disclosure. Specific examples of components and arrangements are described below to simplify the present disclosure. These are, of course, merely examples and are not intended to be limiting. In addition, the present disclosure may repeat reference numerals and/or letters in the various examples. This repetition is for the purpose of simplicity and clarity and does not in itself dictate a relationship between the various embodiments and/or configurations discussed. Moreover, the formation of a feature on, connected to, and/or coupled to another feature in the present disclosure that follows may include embodiments in which the features are formed in direct contact, and may also include embodiments in which additional features may be formed interposing the features, such that the features may not be in direct contact. In addition, spatially relative terms, for example, "lower," "upper," "horizontal," "vertical," "above," "below," "up," "down," "top," "bottom," etc. as well as derivatives thereof (e.g., "horizontally," "downwardly," "upwardly," etc.) are used for ease of the present disclosure of one features relationship to another feature. The spatially relative terms are intended to cover different orientations of the device including the features.

FIG. 1 is a flowchart of an exemplary method of forming a through-silicon-via (TSV) opening through a substrate. FIGS. 2A-2D are schematic cross-sectional views of forming a TSV opening in an integrated circuit during various fabrication stages. It is understood that FIGS. 1 and 2A-2D have been simplified for a better understanding of the concepts of the present disclosure. Accordingly, it should be noted that additional processes may be provided before, during, and after the methods of FIGS. 1 and 2A-2D, and that some other processes may only be briefly described herein.

Referring now to FIG. 1, the method 100 can include forming a TSV opening through a substrate (block 110). The method 100 can include removing a recast of a material of the substrate on the sidewalk of the TSV opening with a first chemical (block 120). The method 100 can also include cleaning the sidewalls of the TSV opening with a second chemical by substantially removing a residual of the first chemical (block 130).

For example, an integrated circuit 200 can include a substrate 201 as shown in FIG. 2A. In some embodiments, the integrated circuit 200 may include various passive and active microelectronic devices (not shown), such as resistors, capacitors, inductors, diodes, metal-oxide-semiconductor field effect transistors (MOSFETs), complementary MOS (CMOS) transistors, bipolar junction transistors (BJTs), laterally diffused MOS (LDMOS) transistors, high power MOS transistors, FinFET transistors, other types of transistors, and/or any combinations thereof. In other embodiments, the integrated circuit 200 is used for light emitting diodes (LEDs).

In some embodiments, the substrate 201 may include an elementary semiconductor including silicon or germanium in crystal, polycrystalline, or an amorphous structure; a compound semiconductor including silicon carbide, gallium



arsenic, gallium phosphide, indium phosphide, indium arsenide, and/or indium antimonide; an alloy semiconductor including SiGe, GaAsP, AlInAs, AlGaAs, GaInAs, GaInP, and/or GaInAsP; any other suitable material; or combinations thereof. In at least one embodiment, the alloy semiconductor substrate may have a gradient SiGe feature in which the Si and Ge composition change from one ratio at one location to another ratio at another location of the gradient SiGe feature. In another embodiment, the alloy SiGe is formed over a silicon substrate. In another embodiment, a SiGe substrate is strained. Furthermore, the semiconductor substrate may be a semiconductor on insulator, such as a silicon on insulator (SOI), or a thin film transistor (TFT). In some examples, the semiconductor substrate may include a doped epitaxial (epi) layer or a buried layer. In other examples, the compound semiconductor substrate may have a multilayer structure, or the substrate may include a multilayer compound semiconductor structure.

Referring to FIG. 2A, in some embodiments a dielectric layer **205** can be formed over a surface **201a** of the substrate **201**. In other embodiments, a dielectric layer **203** can be formed adjacent to another surface **201b** of the substrate **201**. The dielectric layers **203** and **205** can each include at least one material, such as silicon oxide, silicon nitride, silicon oxynitride, silicon carbide, silicon oxycarbide, silicon oxynitride, other dielectric materials and/or any combinations thereof. The dielectric layers **205** and **203** can protect the surfaces **201a** and **201b**, respectively, from being activated by a chemical during a removal process **220** described below in conjunction with FIG. 2C.

In some embodiments, the method **100** can optionally include coating a water soluble layer (not shown) over each of the dielectric layers **203** and/or **205**. The water soluble layer is provided to prevent particles generated from a drilling process described below in conjunction with FIG. 2B falling on the dielectric layers **203** and **205**.

Referring to FIG. 2B, the method **100** can form a TSV opening **215** through the substrate **201**. In some embodiments including the dielectric layers **203** and/or **205**, the TSV opening **215** is also formed through the dielectric layers **203** and/or **205**. The TSV opening **215** can be formed by, for example, a laser drilling, a mechanical drilling, a chemical etching process, or any other drilling processes. In some embodiments forming the TSV opening **215** by a laser drilling **210**, the laser drilling **210** can use a laser having a wavelength of about 355 nanometer (nm) or less. The laser source can be a neodymium-doped yttrium aluminium garnet (Nd:YAG) laser source. The source power of the laser drilling **210** can be about 10.8 Watts or more. The laser drilling **210** can have a repetition rate of about 100 KHz and a pulse duration ranging from about 20 ns to about 75 ns. In some embodiments, the laser drilling **210** can be referred to as a laser ablation.

In some embodiments forming the TSV opening **215** by the laser drilling **210**, a recast **213** can be formed on each sidewall of the TSV opening **215** as shown in FIG. 2B. During the laser drilling **210**, the energy of the laser melts the material, e.g., silicon, of the substrate **201**. The melted silicon is then cooled down, transforming into the amorphous silicon recasts **213**. The TSV opening **215** having the recasts **213** on the sidewalls may cause an hourglass shape and/or rough sidewall surfaces.

Referring to FIG. 2C, the method **100** can include a removal process **220** to remove the recasts **213** of the material of the substrate **201** on the sidewalls of the TSV opening **215** with a chemical. In some embodiments, the chemical can comprise a halogen-containing chemical, e.g., xenon difluoride (XeF<sub>2</sub>), sulfur tetrafluoride sulfur hexafluoride (SF<sub>6</sub>), other halogen-containing chemicals, and/or any combina-

tions thereof. The halogen-containing chemical is provided to activate the recast **213** so as to substantially remove the recast **213** to smoothen the sidewalls **215a** of the TSV opening **215**. In some embodiments using XeF<sub>2</sub>, the removal process **220** can have a flow rate of about 22 standard cubic centimeter per minute (sccm), a processing time of about 120 seconds or more, and a processing temperature of about 35.degree.C. or more.

Though showing that the laser drilling **210** and the removal process **220** are performed in different steps, the scope of this application is not limited thereto. In some embodiments, the removal gas of the removal process **220** can be supplied during the laser drilling process.

As described above in conjunction with FIG. 2A, the method **100** can optionally include coating a water soluble layer (not shown) over the dielectric layers **203** and/or **205**. As noted, particles and/or debris generated from the laser drilling **210** may be sputtered on the water soluble layer. In at least this embodiment, the method **100** can include a process to remove the water soluble layer with deionized water (DI water) so as to remove particles and/or debris on the water soluble layer.

In some embodiments, during and/or after the removal process **220** at least one residual, e.g., residuals **223** may remain on the sidewalls **215a** of the TSV opening **215** as shown in FIG. 2C. Referring to FIG. 2D, the method **100** can include a cleaning process **230** to clean the sidewalls **215a** of the TSV opening **215** with a chemical by substantially removing the residual **223** (shown in FIG. 2C). For example, the residuals **223** may be halogen-containing residuals. In some embodiments, the chemical of the cleaning process **230** can include a first component that is substantially inactive with the material of the substrate **201** and a second component that is substantially active with the halogen component of the halogen-containing chemical. In other embodiments, the first component is selected from a group consisting of helium, neon, argon, krypton, xenon and radon, The second component comprises hydride.

For example, the chemical of the removal process **220** includes XeF<sub>2</sub>. The chemical of the cleaning process **230** comprises xenon dihydride (XeH<sub>2</sub>). The xenon component of XeH<sub>2</sub> is substantially inactive with the material of the substrate **201**. The hydride component (H<sup>+</sup>) of XeH<sub>2</sub> is substantially active with fluorid component (F<sup>-</sup>) of XeF<sub>2</sub>. The hydride component (H<sup>+</sup>) of XeH<sub>2</sub> actively interacts with fluoride component (F<sup>-</sup>) of XeF<sub>2</sub> to form hydrogen fluoride (HF) than can be easily taken away during the cleaning process **230**. In some embodiments, the chemical of the cleaning process **230** can have a flow rate of about 3 standard cubic centimeter per minute (sccm) or more and a concentration of XeH<sub>2</sub> of about 20% or more by volume.

In some embodiments, after the cleaning process **230** a conductive structure (not shown) can be formed in the TSV opening **215**. In some embodiments, the conductive structure can include, for example, a barrier material (e.g., titanium, titanium-nitride, tantalum, tantalum-nitride, other barrier materials, and/or combinations thereof), a conductive material (aluminum, copper, aluminum-copper, polysilicon, other conductive material, and/or combinations thereof), other material that are suitable for forming the conductive structure, and/or any combinations thereof.

In an embodiment of the application, a method of forming a through-silicon-via (TSV) opening includes forming a TSV opening through a substrate. A recast of a material of the substrate on sidewalls of the TSV opening is removed with a first chemical. The sidewalls of the TSV opening are cleaned with a second chemical by substantially removing a residue of the first chemical.

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The foregoing outlines features of several embodiments so that those skilled in the art may better understand the aspects of the present disclosure. Those skilled in the art should appreciate that they may readily use the present disclosure as a basis for designing or modifying other processes and structures for carrying out the same purposes and/or achieving the same advantages of the embodiments introduced herein. Those skilled in the art should also realize that such equivalent constructions do not depart from the spirit and scope of the present disclosure, and that they may make various changes, substitutions, and alterations herein without departing from the spirit and scope of the present disclosure.

What is claimed is:

1. A method, comprising:
  - forming an opening in a substrate, the opening completely extending through the substrate, wherein a recast material is formed on sidewalls of the substrate exposed by the opening;
  - applying a first chemical in the opening to remove the recast material, wherein a residue of the first chemical remains on portions of the sidewalls after the applying of the first chemical; and
  - applying a second chemical in the opening to remove the residue of the first chemical, wherein the second chemical is different from the first chemical, wherein the second chemical contains a first component being substantially inactive with the substrate and a second component being substantially active with the material of the first chemical, wherein the first component is selected from the group consisting of helium, neon, argon, krypton, xenon, and radon, and the second component comprises hydride.
2. The method of claim 1, wherein the forming of the opening comprises laser drilling the opening through the substrate.
3. The method of claim 2, wherein the substrate contains silicon, and the recast material is formed by melting the silicon through the laser drilling and cooling the melted silicon.
4. The method of claim 1, wherein the sidewalls of opening is formed in a manner such that they are roughened or have an hourglass shape.
5. The method of claim 1, wherein the first chemical contains a material that activates the recast material.
6. The method of claim 5, wherein the material of the first chemical includes halogen.
7. The method of claim 1, wherein the forming of the opening and the applying of the first chemical are performed simultaneously.
8. The method of claim 1, further comprising forming a water-soluble layer over the substrate before the forming of the opening and removing the water-soluble layer with deionized water after the forming of the opening.
9. The method of claim 1, further comprising forming a conductive structure in the opening after the applying of the second chemical.

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10. A method, comprising:
  - providing a substrate having a first side and a second side opposite the first side;
  - performing a laser ablating process to form an opening that extends from the first side of the substrate to the second side of the substrate, wherein the laser ablation process melts portions of the substrate, thereby leaving a recast material in the opening;
  - removing the recast material with a first chemical, wherein the removing of the recast material leaves a residue of the first chemical in the opening; and
  - removing the residue of the first chemical with a second chemical different from the first chemical, wherein the first chemical contains halogen and the second chemical contains a first component being substantially inactive with the substrate and a second component being substantially active with halogen, wherein the first component is selected from the group consisting of helium, neon, argon, krypton, xenon, and radon, and the second component comprises hydride.
11. The method of claim 10, wherein the removing of the recast material is performed while the laser ablation process is being performed.
12. The method of claim 10, wherein the opening is formed such that the recast material contributes to an hourglass shape of the opening.
13. The method of claim 10, further comprising forming a water-soluble layer over the substrate before the performing of the laser ablation process and removing the water-soluble layer with deionized water after the performing of the laser ablation process.
14. The method of claim 10, further comprising forming a through-silicon-via in the opening after the removing of the residue.
15. A method, comprising:
  - forming a through-silicon-via (TSV) opening in a silicon substrate through a laser process that melts the silicon of the silicon substrate, wherein the melted silicon adheres to a sidewall of the TSV opening after being cooled, thereby giving the TSV opening at least one of: an hourglass shape and roughened sidewall surfaces;
  - removing the melted silicon using a halogen-containing first chemical, wherein the halogen-containing first chemical leaves a residue in the TSV opening;
  - removing the residue of the halogen-containing first chemical with a second chemical, the second chemical containing a first component that is substantially inactive with the silicon substrate; and
  - a second component that is substantially active with halogen; and
  - thereafter forming a conductive material in the TSV opening, wherein the first component is selected from the group consisting of helium, neon, argon, krypton, xenon, and radon, and the second component comprises hydride.

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